

## ORGANIC COMPOUNDS

*Acta Cryst.* (1995). **C51**, 1131–1133

## Vanillin-I

R. VELAVAN, P. SURESHKUMAR, K. SIVAKUMAR  
AND S. NATARAJAN

*Department of Physics, Anna University,  
Madras 600 025, India*

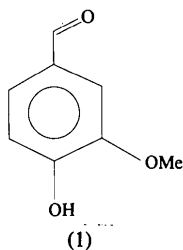
(Received 22 August 1994; accepted 20 October 1994)

## Abstract

Vanillin-I (3-methoxy-4-hydroxybenzaldehyde,  $C_8H_8O_3$ ) crystallizes in a monoclinic crystal system with four molecules in the asymmetric unit. The molecules are linked by  $O-H \cdots O$  hydrogen bonds and form linear chains.

## Comment

Vanillin, (1), occurs stems in nature from a glucoside which hydrolyses to vanillin and sugar. Single crystal growth of vanillin is of considerable interest because of its non-linear optical properties (Singh *et al.*, 1991). Vanillin is said to exist in three polymorphic forms, as studied by McCrone (1950). In the terminology of McCrone (1950), the present structure can be described as vanillin-I. Vanillin crystals, grown by a gel technique (Sureshkumar, Sivakumar & Natarajan, 1994), grow as needles along the crystallographic *b* axis. McCrone (1950) assigned the crystal system as orthorhombic for vanillin-I, based on a powder diffraction pattern with a possible value of  $Z = 8$ . The present study shows that the correct crystal system for vanillin-I is monoclinic.



The bond lengths and angles in the four molecules have normal values. Although the molecule as a whole is planar, there are significant deviations from the mean plane by some atoms. In all four molecules (*A*, *B*, *C* and *D*), the methyl C8 atom deviates the most from the plane of the phenyl ring [in molecule *A* 0.074 (3), *B* 0.056 (4), *C* 0.134 (4) and *D* 0.013 (3) Å].

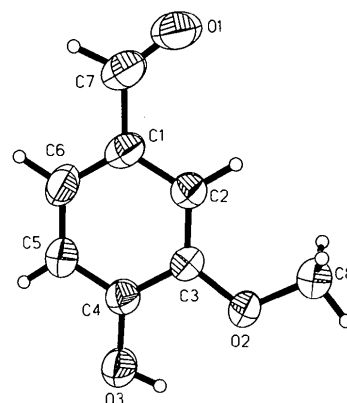


Fig. 1. Structure of a single molecule of vanillin-I with numbering scheme, showing 50% probability displacement ellipsoids.

The four molecules in the asymmetric unit form two pairs lying on two adjacent parallel planes (*A* and *B* in one plane and *C* and *D* in another plane). The dihedral angle between the mean planes of *A* and *B* is 10.22 (8)° and that between those of *C* and *D* is 4.12 (8)°. Each pair is linked by  $O-H \cdots O$  bonds between the hydroxyl group and the O atom of the aldehyde group. The same contacts are extended between the other symmetry-related molecules in their respective planes to form a linear chain.

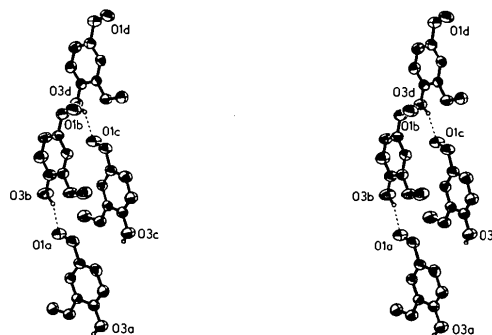


Fig. 2. Stereoview of the four molecules in the asymmetric unit. Hydrogen bonds are shown as dashed lines.

The structures of other vanillin derivatives, isovanillin (3-hydroxy-4-methoxybenzaldehyde) and *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde), also involve  $O-H \cdots O$  hydrogen bonds (Iwasaki, 1973; Iwasaki, Tanaka & Aihara, 1976). While *o*-vanillin has an intramolecular hydrogen bond, isovanillin and vanillin-I involve intermolecular  $O-H \cdots O$  hydrogen bonds and form linear chains of molecules in the crystal lattice.

**Experimental**

Single crystals of vanillin were grown by a gel technique. Details are published elsewhere (Sureshkumar, Sivakumar & Natarajan, 1994).

*Crystal data*

C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	Mo K $\alpha$ radiation
$M_r = 152.14$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
$P2_1$	$\theta = 8-15^\circ$
$a = 14.049 (1) \text{ \AA}$	$\mu = 0.104 \text{ mm}^{-1}$
$b = 7.8740 (8) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 15.017 (1) \text{ \AA}$	Needle
$\beta = 115.45 (1)^\circ$	$0.5 \times 0.4 \times 0.4 \text{ mm}$
$V = 1499.9 (2) \text{ \AA}^3$	Colourless
$Z = 8$	
$D_x = 1.347 \text{ Mg m}^{-3}$	

*Data collection*

Enraf-Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.0090$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 24.96^\circ$
Absorption correction: none	$h = 0 \rightarrow 16$
2970 measured reflections	$k = 0 \rightarrow 9$
2848 independent reflections	$l = -17 \rightarrow 16$
2139 observed reflections	2 standard reflections monitored every 100 reflections
$[I > 2\sigma(I)]$	intensity decay: <2%

*Refinement*

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.093 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.0250$	$\Delta\rho_{\text{min}} = -0.085 \text{ e \AA}^{-3}$
$wR(F^2) = 0.0603$	Extinction correction:
$S = 1.066$	$F_c^* = kF_c[1 + (0.001\chi \times F_c^2 \lambda^3 / \sin 2\theta)]^{-1/4}$
2848 reflections	Extinction coefficient:
526 parameters	$\chi = 0.0110 (10)$
All H-atom parameters refined	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
C1A	-0.5353 (2)	-0.1403 (3)	-0.1898 (2)	0.0522 (6)
C2A	-0.6376 (2)	-0.1900 (3)	-0.2551 (2)	0.0474 (5)
C3A	-0.6984 (2)	-0.2800 (3)	-0.2202 (1)	0.0431 (5)
C4A	-0.6580 (2)	-0.3225 (3)	-0.1203 (1)	0.0485 (5)
C5A	-0.5578 (2)	-0.2711 (4)	-0.0560 (2)	0.0605 (7)
C6A	-0.4971 (2)	-0.1802 (3)	-0.0912 (2)	0.0607 (6)
C7A	-0.4684 (2)	-0.0463 (4)	-0.2247 (2)	0.0649 (7)
C8A	-0.8469 (2)	-0.2927 (4)	-0.3769 (2)	0.0606 (7)
O1A	-0.4922 (1)	-0.0024 (2)	-0.3085 (2)	0.0756 (5)
O2A	-0.7993 (1)	-0.3332 (2)	-0.27468 (9)	0.0555 (4)
O3A	-0.7148 (1)	-0.4128 (3)	-0.0834 (1)	0.0654 (5)
C1B	-0.0811 (2)	0.3711 (3)	-0.2820 (2)	0.0516 (6)
C2B	-0.1194 (2)	0.3109 (3)	-0.2159 (2)	0.0496 (6)
C3B	-0.2175 (2)	0.2403 (3)	-0.2499 (2)	0.0486 (5)
C4B	-0.2801 (2)	0.2283 (3)	-0.3520 (2)	0.0573 (6)
C5B	-0.2421 (2)	0.2893 (4)	-0.4167 (2)	0.0699 (8)

C6B	-0.1427 (2)	0.3592 (4)	-0.3816 (2)	0.0638 (7)
C7B	0.0241 (2)	0.4459 (4)	-0.2465 (2)	0.0614 (6)
C8B	-0.2067 (3)	0.1908 (5)	-0.0895 (2)	0.0745 (8)
O1B	0.0852 (1)	0.4656 (3)	-0.1616 (1)	0.0752 (5)
O2B	-0.2640 (1)	0.1771 (3)	-0.1943 (1)	0.0664 (5)
O3B	-0.3772 (1)	0.1597 (3)	-0.3889 (1)	0.0823 (6)
C1C	-0.0993 (2)	-0.1683 (3)	-0.2131 (2)	0.0520 (6)
C2C	-0.1988 (2)	-0.2257 (3)	-0.2797 (2)	0.0477 (5)
C3C	-0.2641 (2)	-0.3041 (3)	-0.2464 (1)	0.0458 (5)
C4C	-0.2314 (2)	-0.3264 (3)	-0.1445 (1)	0.0501 (5)
C5C	-0.1339 (2)	-0.2682 (4)	-0.0792 (2)	0.0657 (7)
C6C	-0.0686 (2)	-0.1896 (4)	-0.1131 (2)	0.0669 (7)
C7C	-0.0283 (2)	-0.0853 (4)	-0.2471 (2)	0.0644 (7)
C8C	-0.4045 (2)	-0.3334 (6)	-0.4071 (2)	0.0758 (9)
O1C	-0.0445 (1)	-0.0610 (3)	-0.3317 (1)	0.0710 (5)
O2C	-0.3620 (1)	-0.3656 (2)	-0.3034 (1)	0.0617 (5)
O3C	-0.2928 (1)	-0.4023 (3)	-0.1081 (1)	0.0687 (5)
C1D	0.3563 (2)	0.3354 (3)	-0.3111 (2)	0.0515 (5)
C2D	0.3226 (2)	0.2615 (3)	-0.2450 (2)	0.0462 (5)
C3D	0.2240 (2)	0.1904 (3)	-0.2789 (1)	0.0419 (5)
C4D	0.1566 (2)	0.1947 (3)	-0.3800 (2)	0.0465 (5)
C5D	0.1899 (2)	0.2683 (3)	-0.4455 (2)	0.0561 (6)
C6D	0.2894 (2)	0.3377 (4)	-0.4108 (2)	0.0599 (6)
C7D	0.4609 (2)	0.4114 (4)	-0.2760 (2)	0.0637 (7)
C8D	0.2466 (2)	0.1089 (4)	-0.1180 (2)	0.0598 (6)
O1D	0.5264 (1)	0.4147 (3)	-0.1917 (1)	0.0725 (5)
O2D	0.1828 (1)	0.1121 (2)	-0.22245 (9)	0.0541 (4)
O3D	0.0588 (1)	0.1277 (3)	-0.4165 (1)	0.0624 (5)

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

	A	B	C	D
C1—C6	1.377 (3)	1.372 (3)	1.382 (3)	1.383 (3)
C1—C2	1.402 (3)	1.401 (3)	1.399 (3)	1.398 (3)
C1—C7	1.460 (3)	1.462 (3)	1.456 (3)	1.458 (3)
C2—C3	1.375 (3)	1.366 (3)	1.367 (3)	1.373 (3)
C3—O2	1.363 (2)	1.356 (3)	1.360 (2)	1.362 (2)
C3—C4	1.397 (3)	1.405 (3)	1.407 (3)	1.403 (3)
C4—O3	1.353 (3)	1.345 (3)	1.344 (3)	1.350 (3)
C4—C5	1.382 (3)	1.380 (3)	1.376 (3)	1.384 (3)
C5—C6	1.381 (3)	1.378 (4)	1.374 (4)	1.378 (3)
C7—O1	1.205 (3)	1.203 (3)	1.206 (3)	1.204 (3)
C8—O2	1.423 (3)	1.432 (3)	1.431 (3)	1.434 (2)
C6—C1—C2	119.8 (2)	119.7 (2)	119.2 (2)	119.6 (2)
C6—C1—C7	119.2 (2)	119.4 (2)	119.6 (2)	119.8 (2)
C2—C1—C7	121.0 (2)	120.9 (2)	121.2 (2)	120.7 (2)
C3—C2—C1	119.7 (2)	120.4 (2)	120.3 (2)	120.2 (2)
O2—C3—C2	125.9 (2)	126.5 (2)	126.0 (2)	125.8 (2)
O2—C3—C4	114.2 (2)	114.0 (2)	114.1 (2)	114.5 (2)
C2—C3—C4	120.0 (2)	119.6 (2)	119.9 (2)	119.6 (2)
O3—C4—C5	118.1 (2)	118.8 (2)	118.3 (2)	118.1 (2)
O3—C4—C3	121.8 (2)	121.6 (2)	122.1 (2)	121.7 (2)
C5—C4—C3	120.2 (2)	119.7 (2)	119.6 (2)	120.2 (2)
C6—C5—C4	119.7 (2)	120.4 (2)	120.3 (2)	119.7 (2)
C1—C6—C5	120.7 (2)	120.3 (2)	120.7 (2)	120.7 (2)
O1—C7—C1	125.9 (2)	126.0 (2)	126.4 (2)	125.9 (2)
C3—O2—C8	117.6 (2)	117.2 (2)	117.3 (2)	117.1 (2)

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O3B—H3B...O1A	0.89 (4)	2.715 (3)	1.94 (4)	144 (3)
O3D—H3D...O1C	0.84 (3)	2.743 (3)	1.98 (3)	148 (3)
O3A—H3A...O1B <sup>i</sup>	0.85 (2)	2.712 (2)	1.95 (3)	148 (3)
O3C—H3C...O1D <sup>i</sup>	0.88 (3)	2.713 (3)	1.90 (3)	154 (3)

Symmetry code: (i)  $x - 1, y - 1, z$ .

Data were collected using *CAD-4 Software* (Enraf-Nonius, 1989). The structure solution was initially attempted in space group  $P2_1/m$  based on the intensity statistics. An attempt in  $P2_1$  gave four molecules in the asymmetric unit. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by *SHELXL93* (Sheldrick, 1993). All the H

atoms were located from difference Fourier maps and refined isotropically. The program *PARST* (Nardelli, 1983) was used for geometrical calculations and *SHELXTL/PC* (Sheldrick, 1990) for molecular graphics.

The authors thank Dr Fun Hoong Kun, School of Physics, Universiti Sains Malaysia, for molecular graphics facilities. One of the authors (PS) thanks CSIR, India, for the award of a Research Associate Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Iwasaki, F. (1973). *Chem. Lett.* pp. 227–228.
- Iwasaki, F., Tanaka, I. & Aihara, A. (1976). *Acta Cryst.* B32, 1264–1266.
- McCrone, W. C. (1950). *Anal. Chem.* 22, 500.
- Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1990). *SHELXTL/PC. User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Singh, N. B., Heningsen, T., Metz, E. P. A., Hamacher, R., Cumberledge, E., Hopkins, R. H. & Mazelsky, R. (1991). *Mater. Lett.* 12, 270–273.
- Sureshkumar, P., Sivakumar, K. & Natarajan, S. (1994). *Cryst. Res. Technol.* 29, 59–61.

*Acta Cryst.* (1995). C51, 1133–1135

## 4,5-Dihydro-5,5-dimethyl-3H-1,2,4-triazol-3-one 1-Oxide

VIKTOR KETTMANN AND JAN SVĚTLÍK

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, 832 32 Bratislava, Slovak Republic

JOACHIM G. SCHANTL

Institut für Organische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

(Received 13 March 1994; accepted 24 October 1994)

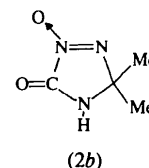
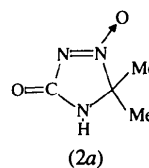
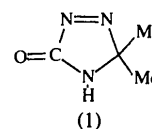
### Abstract

The title compound, C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>, formed by oxidation of the parent 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one,

consists of a planar five-membered ring with the two O atoms displaced slightly on the same side of the ring. Both the azoxy moiety and the amide N atom are involved in conjugation with the carbonyl group. The molecules in the crystal associate into centrosymmetric double-hydrogen-bonded dimers.

### Comment

As part of our studies of heterocyclic azo compounds, we converted 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (1) to the corresponding cyclic azoxy derivative [(2); Schantl, Světlík & Kettmann, 1994] by treatment with peroxytrifluoroacetic acid. Although spectroscopic and analytical data proved the formation of an *N*-oxide, the site of oxygen attachment, *i.e.* which of the N atoms of the azo group was involved, was impossible to determine. The unambiguous identification of the product is important for understanding the mechanism of the oxidative reaction and for making predictions about the reactivity of this novel azoxy derivative. Therefore, to distinguish conclusively between isomers (2a) and (2b) and, at the same time, to establish the detailed molecular structure of this compound, a single-crystal X-ray analysis was undertaken.



The reaction product is shown to be (2a), *i.e.* the oxygen is attached to the N(1) atom. The triazole ring is planar within experimental error ( $\chi^2 = 26$ ) and the O(1) and O(3) atoms are displaced by 0.011 (2) and 0.028 (2) Å, respectively, on the same side of the ring. Comparison of the present structure with that of the parent compound (1) (Schantl, Gstach, Lanznaster, Gieren & Lamm, 1987) shows that on going from compound (1) to compound (2a), the N(1)—N(2) bond length increases from 1.238 (2) to 1.265 (3) Å while the N(2)—C(3) bond is shortened from 1.484 (2) to 1.399 (4) Å, indicating that conjugation between the N=N double bond and the carbonyl group, absent in compound (1), is present in compound (2a). This finding can be interpreted in the following way. In (1), as suggested by Schantl *et al.* (1987), the conjugation is hindered as it would leave the terminal N(1) atom with an unfavourable deficiency of  $\pi$  charge. Consequently, the main factor which triggers the conjugation in compound (2a) appears to be the +M effect of atom O(1), thus extending  $\pi$  delocalization to